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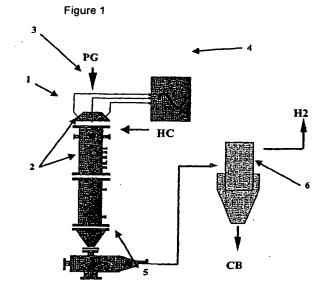
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- (54) Device and method for converting carbon containing feedstock into carbon containing materials, having a defined structure
- (57) Apparatus and process for producing carbon black or carbon containing compounds by converting a carbon containing feedstock, comprising the following steps: generating a plasma gas with electrical energy, guiding the plasma gas through a venturi, whose diameter is narrowing in the direction of the plasma gas flow, guiding the plasma gas into a reaction area, in which under the prevailing flow conditions generated by aerodynamic and electromagnetic forces, no significant recirculation of feedstocks or products into the plasma generating zone occurs, injecting the feedstock into the plasma gas in the reaction area recovering the reaction products from the reaction area and separating carbon black or carbon containing compounds from the other reaction products.



EP 1 188 801 A1

Description

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[0001] The invention relates to a process and apparatus for converting carbon containing feedstock, into carbon black or other carbon containing materials, particularly one having a defined nanostructure.

[0002] More than 99% of the carbon black is presently produced by incomplete combustion processes; the by far dominant one is the « furnace process » developed sixty years ago. Other processes are « channel », « thermal » and « lamp » process. All these industrial processes are characterised by the combustion of about 40% to 60% of the feedstock or raw material to generate the necessary heat to crack the rest of the feedstock. Even though more than 100 different grades of carbon black are currently offered by commercial manufacturers, each grade having different specifications and properties designed to suit particular applications, the production of new materials is limited by the process chemistry (chemical composition, available energy).

[0003] About 6 million MT (metric tons) of carbon black are produced worldwide annually. The raw materials used as feedstock are decant oil for the low quality material (tyre manufacturing), pyrolysis fuel oil (PFO) and coal tar distillates. Pollutant emission resulting from the 12 million MT of oil used to produce the carbon black is 22 million MT CO_2 and millions of MT of SO_X and SO_X . Self-decomposition of acetylene is performed to produce high carbon black grade (40 000 MT) mainly used in battery manufacturing.

[0004] Alternative technology based on electrical plasma as the main energy source was developed at the industrial scale on the basis of a DC carbon electrode plasma generator. PCT/N092/00196 and PCT/N096/00167 disclose such plasma reactors. According to these disclosures, hydrogen is the primary product and carbon material is the secondary product. No evidence has been given that the process can produce carbon black of commercial interest.

[0005] PCT/EP94/00321 discloses a plasma reactor with three electrodes, creating a compound arc by applying an AC current to the electrodes. The feedstock is fed into the reactor by passing it through the arc zone. According to this prior art, the reaction zone, wherein the feedstock is converted into carbon compounds having a defined nanostructure, namely into carbon black, is directly below and adjacent to the arc zone. The feedstock is at least partly circulating through the arc zone. The carbon black produced by this process is a mixture of carbon materials originated by the various heat treatments. This process allows the production of different carbon black materials.

[0006] The objective underlying this invention is therefore to provide a process and apparatus to produce carbon black with well-defined properties, allowing through control of operating conditions and process parameters to obtain high conversion efficiency of feedstock and reproducible product quality.

[0007] According to the invention, this objective is achieved by the process and apparatus defined in the claims. Furthermore, a new carbon black is another embodiment of the invention. Preferred embodiments of the invention are defined in the dependent claims. Features of the invention, combinations or sub-combinations of which constitute additional embodiments thereof, are described in the following and in the specific examples and in the drawing.

[0008] The invention allows control of the operating conditions for the production of carbon black with well-defined properties and prevents circulating of the feedstock and any products through the arc zone thus producing carbon black materials with well defined and consistently reproducible properties. In particular the venturi allows a better control of the reaction temperature and a more efficient mixture in the "low temperature region", the reaction zone, where carbon black is produced.

[0009] A significant advantage of the invention is the possibility to use practically all carbon containing feedstocks. More specifically materials with low combustion enthalpy, e.g. below 80 BMCI, including recycling oil from tyre pyrolisis, can be used as feedstocks.

[0010] The preferred process comprises the following steps: creating a plasma by directing plasma gas through an electric arc, passing or guiding the plasma gas through a venturi zone, whose diameter is narrowing into a throat in the direction of the plasma gas flow, passing or guiding the plasma gas into a reaction zone, having a larger diameter than the throat of the venturi zone, injecting the feedstock into the plasma gas in the reaction zone downstream of the venturi zone (after it has passed the throat of the venturi zone), extracting the reaction products from the reaction zone and recovering the carbon black. It is also possible to inject the feedstock into the throat of the venturi and/or slightly above the venturi.

[0011] The carbon black separated from the other reaction products has a defined nanostructure. This nanostructure morphology and texture is depending on the operating conditions.

[0012] The plasma gas is injected into the reactor space, not necessarily through the plasma arc. In a preferred embodiment, the electric arc is a compound arc, created by at least three electrodes. Preferably, the electrodes are graphite based electrodes and the arc is created by connecting a sufficient AC power source to the electrodes. The current frequency can be the frequency of the grid using a conventional power source (50 - 60 Hz) or it can be higher using a high frequency power switching source. The increase of the frequency can be suitable to increase the arc stability, particularly when using hydrogen as plasma gas. In this case, the current frequency is preferably comprised between 500 Hz to 10 kHz.

[0013] The venturi preferably is made from a graphite based material and is formed as a cone. The downstream side

of the venturi is preferably formed as an edge and therefore building an abruptly expanding zone. An edge between the throat and the abruptly expanding zone causes an abrupt expansion of the plasma gas volume. This is the preferred means to prevent back-flow of carbon containing material into the area upstream of the venturi zone outlet, particularly into the plasma forming region, e.g. into the arc or arcs. The expanding zone also generates a high turbulence zone in the flow that is used to increase the mixing efficiency between the plasma flow and the feedstock and to realize an homogeneous mixture and a better control of the reaction temperature.

[0014] The feedstock may contain or consist of methane, acetylene, ethylene, propylene, C₄-hydrocarbons including butadiene, light or heavy oil, even waste oil and/or pyrolysis fuel oil (PFO), as well as any other material, comprising carbon. Preferably, essentially no oxygen or oxygen containing materials are fed into the arc or into the reactor. Feedstocks containing limited amounts of oxygen in the molecule, e.g. with an atomic ratio of oxygen / carbon of up to 1 / 6 could be used.

[0015] Preferably, the plasma gas is injected axially above the electrodes, in order to pass directly through the arc. The plasma gas itself may preferably comprise or consist of hydrogen, nitrogen, carbon monoxide, argon, helium or any other suitable gas as well as any mixture of the preceding materials, e.g. a mixture of up to 50 vol% CO and hydrogen. The off-gas contains in addition to the plasma gas components essentially solely hydrogen, methane, acetylene and ethylene and thus is relatively independent of the hydrocarbon feedstock. If oxygen compounds are used, some CO and a very small amount of CO₂ are contained in the off-gas.

[0016] Preferably, a part of the off-gas is recycled and used as plasma gas. This is particularly advantageous, if the recycled off-gas is composed essentially solely of hydrogen and traces of hydrocarbons.

[0017] The temperature in the reaction zone is controlled preferably within a range between 900°C and 3000°C, by adjusting the plasma gas flow rate, the electrical energy and the feedstock flow rate.

[0018] The feedstock is injected through at least one injector, preferably through two to five injectors. These injectors can be arranged equally distributed around the circumference of the reaction zone. The injection of the feedstock can be radial towards the center of the plasma gas flow or with a substantial tangential and/or axial component into the outer zone of the plasma gas flow or the reaction zone to generate a vortex-like flow. The injection rate is adjusted to the desired reaction temperature depending on the flow of the hot plasma gas and the nature of the feedstock. A preferred range is 1 to 10 kWh in the plasma gas per 1 kg of carbon in the feedstock.

[0019] The reaction products are of a specifically good quality, when the process is performed without the use of oxygen.

[0020] In one embodiment of the process of the invention, carbon black and hydrogen are produced as useful products. The process of the invention allows the production of a variety of products.

[0021] The method according to the invention is preferably performed in a reactor for converting feedstock, comprising carbon within a plasma into carbon compounds having a defined nanostructure, comprising a chamber with

- (a) a head portion comprising at least two electrodes and a plasma gas supply, for creating an electric arc between the electrodes when a sufficient electric power is supplied, thus creating an arc zone,
- (b) a venturi portion and
- (c) a reaction chamber, comprising at least one feedstock injector,

wherein the venturi portion is placed between the arc zone and the feedstock injector and is narrowing towards the reaction chamber.

The reactor is preferably of cylindrical shape. The chamber itself, at least at its inner surface, may be preferably made from graphite containing material.

[0022] When producing nanostructured carbon material with a process according to the invention, one finds that the structure and quality of the reaction products depends completely on the process parameters, mainly on the reaction temperature and on the residence time, but is surprisingly quite independent of the feedstock. This is the reason, why even methane or waste oil can be used to create high quality carbon materials with a defined nanostructure.

[0023] The invention also provides a new carbon black. This carbon black is characterised by having a negative difference (commonly called "porosity") between nitrogen surface area and CTAB surface area, and an intrinsic density below 1.9, preferably below 1.8, particularly between 1.5 and 1.9 g/cm³. Thus

N₂SA<CTAB SA

especially:

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$-20 \text{ m}^2/\text{g} \le \text{N}_2 \text{SA-CTAB SA} < 0 \text{ m}^2/\text{g}.$

[0024] The preferred carbon black has a nitrogen surface area from 5 to 100 m²/g and a DBP absorption from 30 to 300 ml/100g.

[0025] The new carbon black has the advantage of having a low density. In e.g. tyre applications this results in a reduction of the needed weight of carbon black and in an overall weight reduction of the final rubber product. Another application of the new carbon blacks is in dry cell electrodes.

[0026] The various properties of the carbon black herein claimed and illustrated are measured by the following standard procedures:

Nitrogen surface area (N ₂ SA):	ASTM D3037-93
CTAB SA:	ASTM D3765-92
DPB absorption:	ASTM D2414-93
CDBP absorption:	ASTM D3493
Intrinsic density by Xylene	DIN 12797 (2.5 g carbon black at 15 torr)
lodine number	ASTM D 1510
Sulfur content:	ASTM D 1619
Ash content:	ASTM D1506
pH:	ASTM D1512
Toluene discoloration	ASTM D1618

[0027] Further preferred features and embodiments of the invention are described in the following and with reference to the drawing in which

[0028] Figures 1 to 2 show a preferred embodiment of the reactor of the invention.

[0029] Figure 1 shows schematically a complete reactor set-up for performing the claimed method,

[0030] Figure 2 provides a detailed view of the upper part of the reactor of figure 1.

[0031] Figure 1 shows the reactor 1 comprising a reactor chamber 2 of cylindrical shape, the interior walls are made out of graphite. The head section 3 of the reactor defines the upper end. Three electrodes 8 are mounted at the head section 3, are connected to a power supply 4, being able to deliver a three phase AC current. The current frequency can be the network frequency (50 to 60 Hz) or any higher frequency. The lower end of the reactor chamber 2 is connected to extraction means 5, through which the reaction products are removed from the reactor. These are directed to standard separation means 6 e.g. cyclones and/or filters, wherein the carbon black is separated from hydrogen and other reaction products.

[0032] A more detailed view of the upper part of the reaction chamber 2 is shown in Figure 2. Plasma gas, preferably hydrogen, nitrogen, carbon monoxide, argon or a mixture thereof is fed into the reaction chamber 2 through the centre of head section 3 via an inlet 7. The plasma gas flow rate was adjusted depending on the nature of the plasma gas and the electrical power between 0.001 Nm³.h⁻¹ to 0.3 Nm³.h⁻¹ per kW of electric power. Three graphite electrodes 8 (two are shown in figure 2), connected to the power supply 4, are mounted to the head section 3. The tips of these electrodes are close enough together to ignite an electric compound arc in the presence of the plasma gas, when a sufficient power source is connected to the electrodes. As a result, a plasma is created within the arc zone 9. The temperature of this plasma is controlled by the plasma gas flow and the electric power, supplied to the electrodes 8. The arc zone may be optically controlled through an opening 15. This allows an automatic control of the temperature and/or the quantity of the plasma gas flowing into the reaction zone.

[0033] Below the arc zone 9, a venturi element 11, made of graphite, is located inside the reactor 1. The speed of the plasma gas flow is increased when passing the narrow passage or throat 20 of the venturi element 11.

[0034] The plasma gas then enters the reaction zone 10 after passing the venturi element 11 expanding abruptly, as the lower end of the venturi is formed as a sharp edge and not as a continuous widening section. Into the reaction zone 10, the feedstock is injected through an injector 13, located within the wall 12 of the reactor chamber 2 just below the venturi 11. The injection of the feedstock after the venturi favours the mixing between the plasma gas and the feedstock.

[0035] Preferably, the feedstock is injected through 2 to 5 injectors 13 directly or radially towards the center of the reaction zone 10. Alternatively, the feedstock may also be injected in a more tangential manner, thus entering the reaction zone 10 off centre or with a certain angle co or contra-flow.

[0036] The energy, necessary to control depends upon the reaction process, the flow rate and nature of the feedstock, and is controlled via the plasma gas temperature and/or the plasma gas flow and the power, supplied to the electrodes

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8 by the power supply 4.

[0037] The pressure preferably is slightly above atmospheric pressure to prevent any inleaking of oxygen. The carbon yield may even reach 100% when the input energy (plasma flow plus electrical power) is high enough. Carbon black structure can be decreased by injection of small quantities of alkaline salts. Typically, also a quench zone can be used, where e.g. methane or other suitable quench materials can be introduced.

[0038] In addition to converting carbon containing materials into carbon with a defined nanostructure, hydrogen of good quality is also a useful reaction product, when carrying out the process without the injection of oxygen. This hydrogen may therefore also be separated. Methane or natural gas are particularly attractive feedstocks when the production of carbon compounds, particularly carbon black, and the production of hydrogen are envisaged. Ethane, ethylene, propane, propylene butanes and butylenes are further examples of useful feedstocks.

[0039] In the following examples further preferred features, feature combinations and embodiments of this invention are illustrated.

[0040] The examples were carried out in a reactor set-up substantially as shown in Figures 1 and 2. A plasma power supply employing a three phase electricity source up to 666 Hz with a maximum power of 263 kVA and a current range of up to 400 A was used to supply electricity to three graphite electrodes having their tips at the apices of an isosceles.

Example 1:

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[0041] In the reactor described, a plasma was generated at a nitrogen flow of 9 Nm³.h⁻¹. The plasma was operated at a current of 200 A. As a hydrocarbon feedstock a pyrolysis fuel oil was employed at a flow rate of 2 kg.h⁻¹. The pyrolysis fuel oil (PFO) was fed to the reactor together with an argon carrier gas of 0.5 bar pressure from a tank which was under pressure between 0.75 and 1 bar. The injector was located 2 cm into the graphite reactor wall.

[0042] The carbon black formed was removed in a primary and a secondary filter.

25 Example 2:

[0043] In this example 0.56 Nm³.h⁻¹ of ethylene was used as a feedstock. The plasma used was again a plasma with nitrogen gas at 9 Nm³.h⁻¹ at 200 A. The injection of feedstock done in cycles of 5 minutes; 290 g of carbon black was obtained in the filter.

Example 3:

[0044] In this example, the conditions were similar to the previous example with a continuous injection of ethylene at a rate of 0.56 Nm³/h during 30 minutes.

Example 4:

[0045] In this example, again under process conditions corresponding to those of the previous example. In this experiment ethylene at a rate of 0.56 Nm³.h⁻¹ was injected for sixteen minutes. The plasma gas flow was nitrogen at a rate of 9 Nm³.h⁻¹.

Example 5:

[0046] In this example, again under process conditions corresponding to those of the previous examples. In this experiment methane at a rate of 0.6 Nm³.h⁻¹ was injected for ninety minutes. The plasma gas flow was nitrogen at a rate of 12 Nm³.h⁻¹ and the current 250 A.

[0047] The carbon black obtained from tests according to examples 1 to 5 was tested with respect to the usual properties. The results are shown in table 1. In all examples, the carbon yields were high; it was always possible to reach 100%, e.g. by adjusting energy and feedstock flow.

Table 1:

			•		
	C	arbon black p	roperties		
	Example 1	Example 2	Example 3	Example 4	Example 5
BET(m²/g)	69	75.1	74.6	76	69
CTAB(m²/g)		95.7	90.9		

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Table 1: (continued)

	С	arbon black p	roperties		
	Example 1	Example 2	Example 3	Example 4	Example 5
l ₂ (m ² /g)		95.2	91.9		
DBP(ml/100g)	218	210	224	206	221
CDBP(ml/100g)	94	125	124	127	121
рН	7.5	8.98	8.96	8.86	7.76
Ash (%)	0.08	0.32	0.28	-	
C-yield	100	80	75	85	60
Toluene disc. (%)		72	80	87	
Sulfur	0.04	0.036	0.074		

[0048] The carbon blacks claimed with this invention and obtained by performing the claimed method using the claimed apparatus were tested in standard rubber compositions ASTM 3191 and in typical battery electrode applications in addition. Tables 2 to 6 show the data, resulting from those tests.

[0049] The carbon blacks IRB#7, N-234 and Ensaco 250 are standard carbon blacks. Their properties are presented also in order to allow a comparison with the carbon blacks according to the invention. These are shown as Examples A to D, whereas Example D is the same carbon black as the one of example 1 of table 1. The carbon blacks of examples A to C have been obtained with slightly different process conditions.

Table 2

Carbon Black	IRB#7, N-234	Ensaco 250	Example A	Example B	Example C	Example D (equals Example 1 of table 1)
Process	Furnace	МММ	Plasma	Plasma	Plasma	Plasma
Feedstock	Decant, PFO, Coal tar	PFO	CH4	C8H8	C2H4	PFO

Table 3

Carbon black	IRB#7	N-234	Ensaco 250	Ex. A	Ex. B	Ex. C	Ex. D
Nitrogen S.A. (m ² /g)	80	125	65	65	52	80	69
DBP Abs. (ml/100g)	102	125	190	157	153	232	218

Viscosity and rheometer data

[0050]

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Table 4

Carbon black	IRB#7	N-234	Ensaco 250	Ex. A	Ex. B	Ex. C	Ex. D
ML 1+4, 100 °C	83.6	98.3	103.4	85	73.4	107	F

Table 4 (continued)

Carbon black	IRB#7	N-234	Ensaco 250	Ex. A	Ex. B	Ex. C	Ex. D
		Rhed	ometer at 160 °	С	•	···	•
Min. Torque (dNm)	2.91	3.71	4.11	3.03	2.36	4.34	2.77
Max. Torque (dNm)	21.27	26.62	23.42	22.61	19.48	26.59	22.37
Δ Torque (dNm)	18.36	22.91	19.31	19.58	17.12	22.25	19.60
T90 (minutes)	14.5	14.96	20	9.34	15.56	9.57	14.21

Table 5

Carbon black	IRB#7	N-234	Ensaco 250	Ex. A	Ex. B	Ex. C	Ex. D
	Stress	strain on S	2 at 500 mm/m	in	•		
Tensile strength Mpa	28.5	31.5	25	23.8	20.4	24.7	21.4
Modulus 100 % (MPa)	3.6	3.5	3.3	3.3	2.6	3.9	3.2
Modulus 200 % (MPa)	10.5	10.3	7.9	8.7	6.4	9.8	7.8
Modulus 300 % (MPa)	19.4	19.8	12.8	14.8	10.9	15.9	13.1
Elongation at break (%)	426	443	571	490	551	508	499
			-				
Shore A	70	72	70	69	64	73	67
						-	
Rebound (%)	46.2	41.4	41	47.4	51.3	42.9	51.8
Electrical resistivity (Ohm.cm)	600. 10 ³	240. 10 ³	12.5	1.4 10 ³	106	165, 10 ³	

Table 6

Battery evaluation*	Carbon black - Example 4	Battery carbon black - Super P
Open circuit voltage (V)	1.652	1.654
Short circuit current (A)	9	10.7
Time to 1.1 V (hours)	7.42	8.53
Time to 0.9 V(hours)	11.63	12.63

*R20 type battery having the following composition:

- MnO2 - 50.73 %

- NH4Cl- 1.92% - Carbon black - 10.79 %

- ZnO - 0.64 %

- ZnCl2 - 9.27 % - H2O - 26.63 %

- HgCt2 - 0.03 %

Claims

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- 1. Process for producing carbon black or carbon containing compounds by converting a carbon containing feedstock, comprising the following steps:
 - generating a plasma gas with electrical energy,

- guiding the plasma gas through a venturi, whose diameter is narrowing in the direction of the plasma gas flow,
- guiding the plasma gas into a reaction area, in which under the prevailing flow conditions generated by aerodynamic and electromagnetic forces, no significant recirculation of feedstocks or products into the plasma generating zone occurs,
- injecting the feedstock into the plasma gas in the reaction area
- recovering the reaction products from the reaction area and
- separating carbon black or carbon containing compounds from the other reaction products.
- 2. Method according to claim 1, wherein plasma gas is generated by directing plasma gas through an electric arc, preferably a compound arc, created by at least three electrodes.
 - 3. Method according to claim 1 or 2, characterized by one or more of the following features:
 - (a) The plasma is generated with electrodes comprising graphite;
 - (b) the arc is created by connecting an AC power source to electrodes;
 - (c) the current frequency is comprised between 50 Hz to 10 kHz
 - (d) the venturi comprises graphite at its inner surface;
 - (e) the venturi is formed as a continuous on stepped cone;
 - (f) a venturi is used having a downstream end which abruptly expands from the venturi throat;
 - (g) the feedstock is selected from one or more of methane, ethane, ethylene, acetylene, propane, propylene, heavy oil, waste oil, pyrolysis fuel oil, the feedstock being fed with or without a carrier gas and with or without preheating;
 - (h) the feedstock is a solid carbon material injected together with a carrier gas selected from one or more of carbon black, acetylene black, thermal black graphite, coke or any solid carbon material;
 - (i) metal catalyst, preferably Ni, Co, Fe, is added to the feedstock
 - (j) the plasma gas is injected axially above the center of the electrodes, in order to pass directly through an arc in the arc zone;
 - (k) the gas to produce the plasma gas comprises or consists of one or more of hydrogen, nitrogen, argon, carbon monoxide, helium;
 - (I) the feedstock is a hydrocarbon and the temperature in the reaction zone is between 900°C and 3000°C;
 - (m)the feedstock is a solid carbon and the temperature in the reaction zone is between 3000°C and 5000°C;
 - (n) the plasma gas flow rate is adjusted, depending on the nature of the plasma gas and the electrical power, between 0.001 Nm³/h to 0.3 Nm³/h per kW of electric power;
 - (o) a portion of the off-gas from the reaction is recycled as at least a portion of the gas for generating the plasma gas;
 - (p) the feedstock is injected through at least one injector, preferably through two to five injectors;
 - (q) the feedstock is injected towards the center of the plasma gas flow;
 - (r) the feedstock is injected with a tangential and/or with a radial and/or with an axial component into the outer zone of the plasma gas flow;
 - (s) the process is carried out in the absence of oxygen or in the presence of small quantity of oxygen, preferably

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an atomic weight ratio of oxygen / carbon of less than 1 / 6;

- (t) the process is carried out in the presence of added alkali to decrease structure;
- 5 (u) one or more of the following products is recovered:
 - carbon black;
 - fullerenes:
 - hydrogen;

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- single wall nanotubes
- multi-walls nanotubes
- 4. Reactor to carry out the process of one of the claims directed to processes comprising in open flow communication
- a head part (3), comprising
 - at least two electrodes (8) and
 - a gas supply

for creating an electric arc between the electrodes when a sufficient electric power is supplied, thus creating an arc zone, into which the gas from the gas supply can be fed to generate a plasma gas

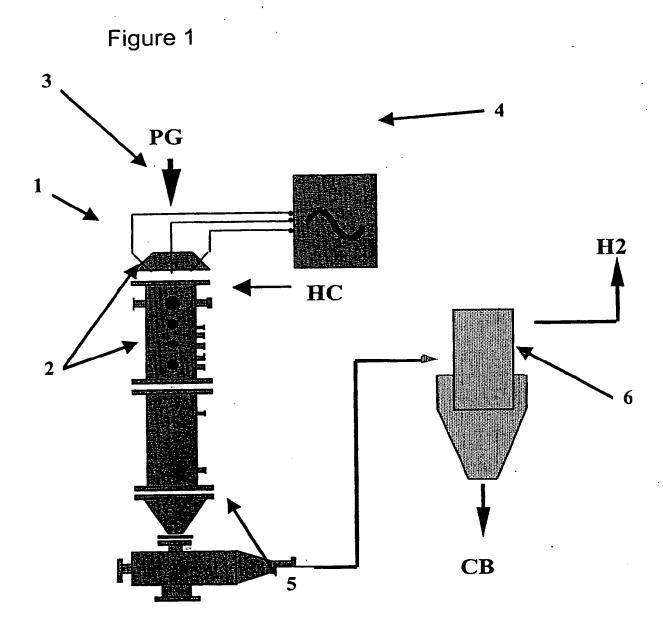
- a venturi shaped choke (11)
- · a reaction section (10) and
- at least one feedstock injector, (3) for feedstock gas injection into the reaction

wherein the venturi is narrowing towards the reaction section.

- 5. Reactor according to claim 4, having substantially interior cylindrical shape.
- 30 6. Reactor according to claim 4 or 5, wherein the high temperature exposed surfaces are from graphite containing high temperature resistant material.
 - 7. Reactor according to claims 4, 5 or 6 comprising a chamber with a height between 1.5 and 5 m and a diameter between 20 and 150 cm.
 - 8. A carbon black having a negative difference between nitrogen surface area and CTAB surface area, and an intrinsic density of less than 1.9 g/cm³, preferably between 1.5 and 1.8 g/cm³.
- Carbon black in accordance with claim 8 having a nitrogen surface area from 5 to 150 m²/g and a DBP absorption
 from 30 to 300 ml/100g.
 - 10. Carbon black in accordance with claim 8 or 9 having a porosity defined by the following range:

 $-20 \text{ m}^2/\text{g} \le \text{N}_2\text{SA-CTAB SA} < 0 \text{ m}^2/\text{g}$

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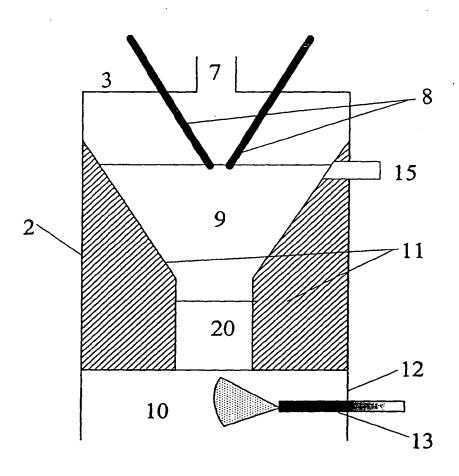


Figure 2



EUROPEAN SEARCH REPORT

Application Number

EP 00 12 0115

Category	Citation of document with of relevant par	indication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InLCI.7)
Ą	FR 2 764 280 A (SC 11 December 1998 (* the whole docume	1998-12-11)	1-7	C09C1/48 C01B31/02 B01J19/08 B01J19/26
A			1-7	B01J19/02 C09C1/56
A	US 3 288 696 A (OR 29 November 1966 (* the whole docume	1966-11-29)	1-7	
A	PATENT ABSTRACTS OF vol. 1995, no. 02, 31 March 1995 (1999) & JP 06 322615 A (1991) 22 November 1994 (1991) * abstract *	5-03-31) NEC CORP),	3	
x	US 5 110 576 A (SOI 5 May 1992 (1992-09 * column 9, line 18 *		2 8-10	TECHNICAL FIELDS SEARCHED (Im.CI.7) CO9C CO1B BO1J
	WO 93 20154 A (HOX (NO); LYNUM STEINAR (NO)) 14 October 19 * examples 1-7 *	KETIL ;HUGDAHL JAN R (NO); KVAERNER ENG 193 (1993-10-14)	8-10	
	US 5 527 518 A (HO) 18 June 1996 (1996- * abstract * * examples 1-7 *		8-10	
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